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The ESTIMATION of LEAD, NICKEL, and ZINC by PRECIPITATION as OXALATES and TITRATION with POTASSIUM PERMANGANATE.

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Art. XXIX.—*The Estimation of Lead, Nickel, and Zinc by Precipitation as Oxalates and Titration with Potassium Permanganate*; by H. L. Ward.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxix.]

Determination of Lead.

Reis in some investigations on the use of oxalates in analysis precipitated lead as the oxalate* by adding ammonium oxalate to a neutral solution of a lead salt and breaking up the resulting soluble double oxalate with a large excess of acetic acid. The insoluble lead oxalate was filtered off and ignited, and the lead was weighed as the oxide. It was thought that lead oxalate precipitated under these conditions might be of such composition that titration with permanganate would give a true estimate of the amount of lead present.

In the experiments of Table I the oxalate was precipitated by the addition of solid ammonium oxalate to the boiling solution of lead nitrate, containing the amount of acetic acid specified. The precipitate was collected on asbestos in a perforated crucible, and washed with small amounts of water. The oxalic acid was then set free by treatment with warm dilute sulphuric acid and titrated with potassium permanganate.

Table I.

The Determination of Lead by Precipitation with Ammonium Oxalate in the Presence of Strong Acetic Acid.

Lead present as the nitrate grm.	Volume at precipitation cm^3	Acetic acid present cm^3	Ammonium oxalate grm.	Lead found grm.	Error grm.
0·0050	100	25	3	0·0016	−0·0036
0·0250	100	25	3	0·0246	−0·0004
0·0500	100	5	3	0·0454	−0·0046
0·0500	100	10	3	0·0480	−0·0020
0·0500	100	25	3	0·0496	−0·0004
0·0500	200	50	7	0·0477	−0·0023
0·0050	100	50	4	0·0048	−0·0002
0·0050	100	50	4	0·0045	−0·0005
0·0250	100	50	4	0·0256	+0·0006
0·0250	100	50	4	0·0250	±0·0000
0·0500	100	50	4	0·0505	+0·0005
0·1000	200	100	8	0·1002	+0·0002

It will be noticed in the first part of the table, where the amount of acetic acid does not exceed one-fourth of the solution, that precipitation is incomplete. If, however, glacial acetic acid makes up one-half the volume of the solution the results are accurate.

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* Ber. Dtsch. Chem. Ges., xiii, 502.

Oxalic acid has been used as a precipitant for lead by a number of investigators.[*] The determinations of Table II were made by adding crystallized oxalic acid to a boiling solution of lead nitrate, filtering, washing, and titrating the oxalate with permanganate as before. When no acetic acid is present, precipitation is not quite complete, but the errors are much less than when ammonium oxalate is used as a precipitant, as may be seen from a comparison with Table I. Acetic acid added in equal volume to the solution secures complete precipitation even in the presence of considerable amounts of ammonium or potassium salts, provided the amount of lead salt present is not too small.

TABLE II.

The Determination of Lead as Oxalate by Precipitation with Oxalic Acid in the Presence of strong Acetic Acid.

Lead present as nitrate	Volume at precipitation	Acetic acid	Oxalic acid	Salts present	Lead found	Error
grm.	cm^3	cm^3	grm.	grm.	grm.	grm.
0·0500	50	--	2	--	0·0491	−0·0009
0·0500	100	--	4	--	0·0488	−0·0012
0·1000	50	--	2	--	0·0994	−0·0006
0·1000	100	--	4	--	0·0990	−0·0010
0·0050	50	25	1	--	0·0050	+0·0000
0·0250	50	25	1	--	0·0256	+0·0006
0·1000	100	50	2	--	0·1002	+0·0002
Potassium Acetate present						
0·1000	50	--	2	·2	0·0962	−0·0038
0·1000	100	--	4	·2	0·0988	−0·0012
0·1000	100	50	2	·2	0·0997	−0·0003
0·1000	100	50	2	·2	0·1000	±0·0000
Ammonium Acetate present						
0·0050	50	25	1	3·	0·0040	−0·0010
0·0250	100	50	2	5·	0·0227	−0·0023
0·1000	100	50	2	2·	0·1000	±0·0000

[†] Böttiger & Pollatz, Chemical Abstracts, ii, 645 ; Mohr-Classen, Lehrbuch der Chemische Analytische Titermethode, 228 ; Low, Jour. Amer. Chem. Soc., xxx, 587.

Determination of Nickel.

Classen has shown* that nickel may be completely precipitated by treating the soluble nickel potassium oxalate with a large amount of acetic acid. The oxalate formed under these circumstances may be ignited to the oxide and weighed as such. It seemed desirable to determine whether this oxalate is of such composition as to allow the estimation of nickel by titrating the oxalate radical with potassium permanganate. The procedure first tried was that recommended by Classen. To a solution of a known amount of nickel sulphate was added a considerable excess of potassium oxalate and the liquid heated to boiling, when the oxalate first formed went into solution as nickel potassium oxalate. Two volumes of acetic acid were then added to precipitate the nickel oxalate. It was found necessary, in order to secure a product which could be filtered, to heat the acetic acid and to run slowly, with constant stirring, into the boiling solution of the double salt. Upon this treatment a flocky precipitate formed, which on standing for some time at 60°–70° went over to a fine powder. By filtration and titration with permanganate it was discovered that the oxalate obtained under these conditions had a tendency to include some of the precipitant, causing high results on titration. On ignition also large positive errors were obtained, but if the oxide was washed to remove the potassium carbonate formed, a very good estimation of the amount of nickel present was secured.

It seemed possible that the use of oxalic acid as a precipitant might eliminate the errors due to inclusion, but it was found that if oxalic acid was added to the boiling solution of a nickel salt containing an equal volume of acetic acid, the oxalate formed came down quickly and in an extremely finely divided condition. The first experiment of Table III was made in this manner, but in the majority of instances filtration proved to be impossible. If, however, precipitation was made in water solution and acetic acid added later to throw out the last traces of nickel, the oxalate came out more slowly and in a form suitable for filtration.

The nickel sulphate taken for analysis was dissolved in water and the solution standardized both by precipitation as nickelic hydroxide and ignition to the oxide and by throwing out as metallic nickel on the rotating cathode. To a definite amount of this solution, diluted to the required volume and heated to boiling, was added an excess of crystallized oxalic acid. Upon cooling, acetic acid was run in and the precipitate allowed to settle over night. The smaller amounts of nickel did not come out from the water solution, and even after adding acetic acid it was necessary to heat it to start precipitation. The nickel oxalate was filtered off on asbestos in a perforated crucible and washed with small amounts of water. The crucible was placed in a beaker containing about 25^{cm^3} of dilute (1:4) sulphuric acid and heat applied to effect the solution of the oxalate. The volume of the solution was then made up to about 200^{cm^3} and cobalt sulphate added until a slight pinkish tinge appeared. This procedure, recommended by Gibbs, was necessary to secure a definite end-point, as the green color of the nickel masked the complementary pink of the permanganate. The contents of the beaker were then heated to boiling and titration made in the usual manner. The results appear in Table III. The positive errors may be assigned to two causes, inclusion of the precipitant and uncertainty of end-point when titrating in colored solutions.

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* Classen, Zeitschr. anal. Chem., xvi, 470.

Table III.

The Determination of Nickel by Precipitation with Oxalic Acid and Treatment with Acetic Acid.

Nickel as sulphate grm.	Volume of water solution at precipitation cm³	Oxalic acid grm.	Acetic acid added cm³	Nickel found grm.	Error grm.
0·0503	100	2	50	0·0502	−0·0001
0·0050	100	2	100	0·0054	+0·0004
0·0251	100	2	100	0·0258	+0·0007
0·0503	50	2	100	0·0514	+0·0011
0·0503	100	2	100	0·0502	−0·0001
0·1257	100	2	100	0·1271	+0·0014

Determination of Zinc as the Oxalate.

It was found to be possible to estimate zinc volumetrically as the oxalate by the process already outlined for nickel. In this case, no colored salts being present in the solution on nitration, a more definite end point was secured and the results obtained are much more accurate, as appears in Table IV.

Table IV.

The Determination of Zinc by Precipitation with Oxalic Acid and Treatment with Acetic Acid.

Zinc as acetate grm.	Volume at precipitation cm³	Oxalic acid grm.	Acetic acid cm³	Zinc found grm.	Error grm.
0·0055	100	2	100	0·0056	+0·0001
0·0274	100	2	100	0·0276	+0·0002
0·0548	50	2	50	0·0553	+0·0005
0·0548	100	2	100	0·0550	+0·0002
0·1370	100	2	100	0·1372	+0·0002

The oxalate of zinc obtained by the method of Classen* was contaminated with potassium oxalate and therefore could not be used to determine the amount of zinc present. On ignition and washing of the oxide obtained, it was shown that all the zinc was recovered.

Summary.

Experiments have been given to show that lead may be determined by precipitation, either with ammonium oxalate or oxalic acid, in the presence of large volumes of acetic acid and titration of the oxalate formed with permanganate.

Nickel has been estimated by precipitation by oxalic acid in water solution, the addition of acetic acid to separate the metal remaining in solution, and titration with permanganate. Errors may occur in this method from inclusion of the precipitant or indefiniteness of the end point.

Zinc may be estimated very accurately by the method used for nickel.

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* Classen, Zeitschr. anal. Chem., xvi, 470.

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